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INTERFACIAL CHEMISTRY OF III-V SEMICONDUCTORS FOR PHOTOELECTROCHEMICAL WATER SPLITTING

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Introduction

Photoelectrochemical (PEC) production of H_2 fuel from water and sunlight is a promising long-term, sustainable energy solution.¹ However, intensive screening has failed to discover an electrode material that meets targets for both efficiency and durability. The design difficulty arises from the materials requirements that must be simultaneously met, including efficiency of photon harvesting, as well as favorable thermodynamics and reaction kinetics for photolysis. At present, the most efficient devices are based on III-V semiconductors. For example, tandem devices based on a $GaInP_2$ photocathode have demonstrated solar-to-hydrogen conversion efficiencies in excess of 12%.² However, these devices exhibit rapid photocorrosion in aqueous environments, limiting their practicality.^{3,4}

Ab initio modeling and simulation can provide unique insight into the mechanisms and properties that limit successful operation. However, in order to ensure maximal accuracy and transferability of results, it is crucial that the models properly account for the realistic operating environment of the electrodes. As a step towards this end, we have performed extensive *ab initio* molecular dynamics simulations on $GaP(001)$ and $InP(001)$ surfaces in the presence of liquid water. Our surface models also include oxygen surface adsorbates, which are omnipresent in experimental analyses. We find that even small concentrations of surface oxygen dramatically alter the interfacial structure. In addition, GaP and InP exhibit qualitatively different interfacial dynamics, despite identical crystal structures and very similar electronic properties.

Computational Details

Results are based on density functional theory using the plane-wave pseudopotential formalism as implemented in the Quantum-ESPRESSO code.⁵ The Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional was used.⁶ Semi-core d states were included in the valence description of the pseudopotentials for In and Ga.

Car-Parrinello molecular dynamics results on $InP(001)$ and $GaP(001)$ were obtained using seven-layer (4×4) surface slabs (16 atoms per layer) and an interlayer spacing accommodating 142 D_2O molecules at ambient density. In each case, the In/Ga-rich surface was used, and both surfaces were identically terminated. The fictitious electronic mass was chosen as 700 a.u., using a time step of 12 a.u. All simulations were run within the canonical NVT ensemble at 400 K (boiling temperature is elevated in molecular dynamics simulations). Simulations were run for 20 ps each.

Three representative surfaces were tested for each material: a pristine mixed-dimer $\delta(2 \times 4)$ reconstruction, a surface with oxygen at the bridge sites (0.5 ML oxygen coverage), and a surface with hydroxyl at the bridge and atop sites (1.5 ML coverage). The choice of these particular surfaces was based on a previous analysis of the complex surface chemistry of $GaP(001)$ and $InP(001)$ in the presence of oxygen and hydroxyl.⁷ In particular, it was shown that the fundamental electronic and chemical properties of more complex adsorbate-decorated surfaces could be well described as a mixture of local bond topologies. This ensures that the choice of surfaces is as generally representative as possible.

Results and Discussion

Dissociative Adsorption of Water. The presence of surface oxygen in the dynamics simulations leads to spontaneous dissociative adsorption of water via one of the two mechanisms shown in Figure 1. In each case, the surface oxygen acts as the proton acceptor. The first mechanism involves direct proton transfer between the water and the surface oxygen, whereas the second mechanism uses a water molecule in solution as an intermediary in a Grotthuss-type chain. In contrast, the pristine surface showed no water dissociation. Nudged Elastic Band (NEB) calculations were used to confirm that the barrier for dissociation drops from 0.71-0.82 eV for the pristine surface to 0.04-0.16 for the oxygen-adsorbed surface, assuming Mechanism #1 in Figure 1.

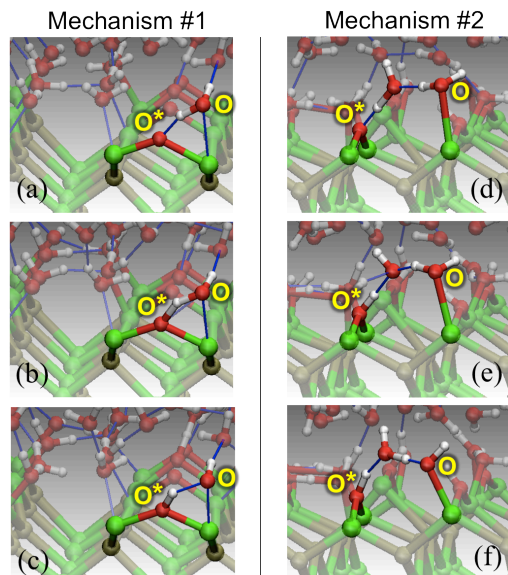


Figure 1. Observed water dissociation mechanisms in $GaP/InP(001)$. Mechanism #1 (a-c) does not have a solution molecule intermediate, whereas #2 (d-f) does. O and O* are the donor and acceptor oxygens.

The result of water dissociation at an oxygen adsorption site is surface hydroxylation, suggesting that the $GaP/InP(001)$ -water interface is predominantly comprised of surface hydroxyl groups. These feature strong hydrogen bonding with liquid water, which qualitatively alters the interfacial structure.

The water dissociation events shown in Figure 1 are representative of a class of proton-transfer events observed on the oxygen- and hydroxyl-covered surfaces. In these events, atop hydroxyl groups can act as proton acceptors in addition to oxygen bridges, forming adsorbed water molecules in the process. Similarly, bridge hydroxyls can act as proton donors, leaving bridge oxygens behind. Such reactions are observed frequently in the dynamics of both GaP and InP .

Interfacial Hydrogen Bonding. If oxygen or hydroxyl is present at the surface, hydrogen bonding between the surface and the surrounding water proves to be unusually strong. This is in part responsible for the observed ease of local proton transfer. However, close analysis reveals that the topology and dynamics of the hydrogen-bond network are quite different for GaP and InP .

The topology of the hydrogen-bond network elements is shown in Figure 2, parameterized by the location of the donor and acceptor oxygens in a given hydrogen bond. The color contours point to the most frequented regions of phase space. It is immediately evident that InP explores a broader overall topological phase space, with more distinct types of bonds. This is particularly true for bonds formed fully within the adsorbate layer, or between the adsorbate layer and the first full solvation layer.

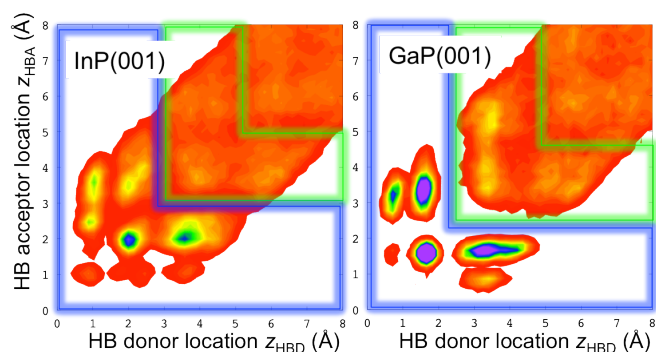


Figure 2. Topological phase-space contours of hydrogen bonds at the InP/GaP-water interface, parameterized by the distance of the donor/acceptor pair from the interface. Purple is the region of highest density. Blue and green outlines indicate the adsorbate and first solution layers.

Equally significantly, the regions of phase space corresponding to different hydrogen bond topologies are connected in the case of InP but discrete and disconnected in the case of GaP. Physically, connectivity of these regions is related to the ability of the system to interchange between different overall network topologies. According to Figure 2, InP is able to dynamically reconfigure its interfacial hydrogen-bond network in a way that is kinetically inhibited for GaP. This does not indicate that the hydrogen-bond network for GaP is static. In fact, hydrogen bond breaking is frequently observed for both surfaces. However, it does indicate that when hydrogen bonds are broken and reformed on GaP, the new configuration does not *topologically* differ from the original.

The results of Figure 2 point to an InP-water interface that is substantially more fluid and dynamic than the GaP-water interface. This is easily seen upon direct observation of the interfacial dynamics trajectories. This may seem surprising, given the electronic and structural similarities between GaP and InP. The reason can be traced to two factors. First, the In-In surface vibrational modes are softer due to the larger mass of In with respect to Ga. This allows the bonds between surface atoms and adsorbates to explore a wider variety of interatomic angles and bond lengths, and thus a wider variety of topological configurations. Second, the Ga-O bond has higher covalent character and overall strength than the In-O bond. This keeps the oxygen directionally confined and makes bond rearrangement more difficult.

Potential Implications

Long-range proton transport. Local proton hopping can translate to long-range surface proton transport if it is accompanied by rapid, facile reorganization of the hydrogen-bond network. If, on the other hand, the network remains largely static on the timescale of proton hopping, then the proton transfer events will remain local, confined to exchanges among a small number of similar configurations.

InP explores a broader topological phase space of hydrogen bonding with greater efficiency than does GaP. Accordingly, we conclude that only InP should readily exhibit long-range surface proton transport. It is worth noting that because the local proton hops are so frequent, surface proton transport is actually faster than proton conduction through the liquid. For GaP, this same process is kinetically hindered.

Dynamical Surface Passivation. It is known that InP displays some native photocorrosion resistance when coated with a thin oxide layer.⁴ However, GaP does not (nor does the alloy material GaInP₂).⁸ The reason for this is not well understood, given the similarities between the two materials.

Our results offer a possible explanation for the discrepancy that is grounded in the differences in the surface dynamics. The proposed corrosion resistance mechanism is shown schematically in Figure 3. Because corrosion competes kinetically with hydrogen evolution in III-V phosphides, the reaction chemistry will generally be dominated by the faster of the two processes. Assuming dangling surface bonds act as carrier traps and nucleation sites for photocorrosion, as has been suggested,⁷ then corrosion can be inhibited by rapidly passivating these sites as they are formed. Here, long-range proton transport becomes valuable, because it can be used to supply hydrogen for site passivation (e.g., by surface diffusion from the water dissociation site to the dangling-bond site). The surface conduction mechanism is faster than in liquid water, making the kinetic competition with corrosion more favorable than it would otherwise be.

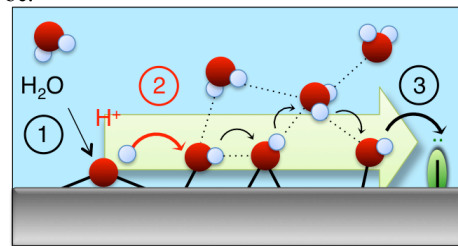


Figure 3. Schematic of the proposed passivation mechanism. Water dissociation (1) leads to H⁺ transport (2) to a dangling bond site (3).

Conclusions

We have shown that including the presence of surface oxygen-derived adsorbates in a dynamical model of the GaP/InP(001)-water interface is crucial for capturing the interfacial chemistry. Surface oxygen acts as a proton acceptor, permitting dissociative adsorption of water at the surface. The result is rapid surface hydroxylation, which nucleates the formation of a well-defined interfacial hydrogen-bond network. The dynamics of this network are quite different for InP and GaP. This allows local proton hops to manifest as long-range hydrogen transport in InP but not in GaP. We suggest that the differences in the interfacial dynamics may be responsible for observed differences in native photocorrosion resistance between partially oxidized surfaces of the two species.

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